CHAPTER THREE

INORGANIC ANALYTES

Prior to employing the methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

3.1 SAMPLING CONSIDERATIONS

3.1.1 Introduction

This manual contains procedures for the analysis of inorganic analytes in a variety of matrices. These methods are written as specific steps in the overall analysis scheme -- sample handling and preservation, sample digestion or preparation, and sample analysis for specific inorganic components. From these methods, the analyst must assemble a total analytical protocol which is appropriate for the sample to be analyzed and for the information required. This introduction discusses the options available in general terms, provides background information on the analytical techniques, and highlights some of the considerations to be made when selecting a total analysis protocol.

3.1.2 Definition of Terms

Optimum concentration range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

Sensitivity: (a) Atomic Absorption: The concentration in milligrams of metal per liter that produces an absorption of 1%. (b) Inductively Coupled Plasma (ICP): The slope of the analytical curve, i.e., the functional relationship between emission intensity and concentration.

Method detection limit (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing the analyte which has been processed through the preparative procedure.

Total recoverable metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Method 3005).

Dissolved metals: The concentration of metals determined in a sample after the sample is filtered through a 0.45-μm filter (Method 3005).

Suspended metals: The concentration of metals determined in the portion of a sample that is retained by a 0.45-μm filter (Method 3005).

Total metals: The concentration of metals determined in a sample following digestion by Methods 3010, 3015, 3020, 3050, 3051, or 3052.

Instrument detection limit (IDL): The concentration equivalent to a signal due to the analyte which is equal to three times the standard deviation of a series of 7 replicate measurements of a reagent blank's signal at the same wavelength.

Interference check sample (ICS): A solution containing both interfering and analyte elements of known concentration that can be used to verify background and inter-element correction factors.

Initial calibration verification (ICV) standard: A certified or independently prepared solution used to verify the accuracy of the initial calibration. For ICP analysis, it must be run at each wavelength used in the analysis.

Continuing calibration verification (CCV): Used to assure calibration accuracy during each analysis run. It must be run for each analyte as described in the particular analytical method. At a minimum, it should be analyzed at the beginning of the run and after the last analytical sample. Its concentration should be at or near the mid-range levels of the calibration curve.

Calibration standards: A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

Linear dynamic range: The concentration range over which the analytical curve remains linear.

Method blank: A volume of reagent water processed through each sample preparation procedure.

Calibration blank: A volume of reagent water acidified with the same amounts of acids as were the standards and samples.

Laboratory control standard: A volume of reagent water spiked with known concentrations of analytes and carried through the preparation and analysis procedure as a sample. It is used to monitor loss/recovery values.

Method of standard addition (MSA): The standard-addition technique involves the use of the unknown and the unknown plus one or more known amounts of standard. See Method 7000, for detailed instructions.

Sample holding time: The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

Check Standard: A solution containing a known concentration of analyte derived from externally prepared test materials. The check standard is obtained from a source external to the laboratory and is used to check laboratory performance.

3.1.3 Sample Handling and Preservation

Sample holding times, digestion volumes and suggested collection volumes are listed in Table 3-1. The sample volumes required depend upon the number of different digestion procedures necessary for analysis. This may be determined by the application of graphite-furnace atomic absorption spectrophotometry (GFAA), flame atomic absorption spectrophotometry (FLAA), inductively coupled argon plasma emission spectrometry (ICP), hydride-generation atomic absorption spectrometry (HGAA), inductively coupled plasma mass spectrometry (ICP-MS) or cold-vapor atomic absorption spectrometry (CVAA) techniques, each of which may require different digestion procedures. The indicated volumes in Table 3-1 refer to that recommended for the individual digestion procedures and to that recommended for sample collection volumes. In all cases for waste testing, representative sampling must be maintained.

In the determination of trace metals, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption, and (b) depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis require particular attention. The following cleaning treatment sequence has been determined to be adequate to minimize contamination in the sample bottle, whether borosilicate glass, linear polyethylene, polypropylene, or Teflon: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and reagent water.

> NOTE: **Chromic acid should not be used to clean glassware**, especially if chromium is to be included in the analytical scheme. Commercial, non-chromate products (e.g., Nochromix) may be used in place of chromic acid if adequate cleaning is documented by an analytical quality control program. (Chromic acid should also not be used with plastic bottles.)

3.1.4 Safety

The toxicity or carcinogenicity of each reagent used in these methods has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in these methods. A reference file of material data-handling sheets should also be made available to all personnel involved in the chemical analysis. The following additional references to laboratory safety are available:

1. "Carcinogens - Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

2.   "OSHA Safety and Health Standards, General Industry," 29 CFR 1910.

3.   "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, 51 FR 26660, July 24, 1986.

4. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety.

3.1.5   Sample Preparation

For all non-speciated digestion methods, great reduction in analytical variability can be achieved by use of appropriate sample preparation procedures. Generally the reduction in subsampling variance is accomplished by drying the sample, reducing its particle size, and homogeneously mixing the resulting fines.

Specifically, if the sample can not be well mixed and homogenized on an as received basis, then air or oven drying at 60°C or less, crushing, sieving, grinding, and mixing should be performed as needed to homogenize the sample until the subsampling variance is less than the data quality objectives of the analysis. While proper sample preparation generally produces great reduction in analytical variability, be aware that in certain unusual circumstances there could be loss of volatile metals (e.g. Hg, organometallics) or irreversible chemical changes (e.g., precipitation of insoluble species, change in valence state) caused by inappropriate sample preparation procedures.

Variability inherent in the analytical determinative procedure is assessed by matrix spiking of individually digested samples.   Variability due to sample heterogeneity is assessed by analyzing sample replicates. For most samples, sampling imprecision is much greater than analytical imprecision. Because of this, the greatest advances in environmental monitoring are occurring in the area of sample collection and preparation.

3.1.6   Clean Chemistry and the Analytical Blank

The significant role of the analytical blank in chemical analysis of trace metals cannot be over stressed. Sensitive instrumentation such as inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and graphite-furnace atomic absorption spectrophotometry (GFAA) requires that sample preparation be at least as sophisticated as the instruments used in analysis. The analytical blank is normally a primary source of error in trace element analysis. Trace analysis is as dependent on control of the analytical blank as it is on the accuracy and precision of the instrument making the measurement. Inability to control contamination that is external to the sample, or those contributions of the analyte coming from all other sources than the sample, is frequently the limiting factor in trace (parts per million (ppm) to parts per billion (ppb)) and ultra-trace (ppb to parts per trillion (ppt)) analysis. Analytical blank contributions occur from the following four major sources (Ref. 1-5):

·   the atmosphere in which the sample preparation and analysis are conducted,
·   the purity of the reagents used in sample preparation, including all reagents and the quantities added directly to the sample,
·   the materials and equipment used in digestion or extraction vessels that come in contact with the sample during the sample preparation and analysis, and
·   the analyst's technique and skill in preparing the samples and performing the analyses.

Only under very few circumstances can the analyst ignore the contribution of the uncertainty of the blank when calculating the uncertainty of the overall analytical result. One condition to consider is whether the concentration of the blank is insignificant compared to the analytical level. For example, when the blank value is less than 10^3-10^4 smaller than the sample measurement, the uncertainty of the blank measurement is insignificant compared with the uncertainty of the analytical measurement. This situation only occurs when the blank signal is extremely low

compared to the measurement, which is rarely the case when trace and ultra-trace analyses are conducted. Typically the blank value is significant and must be subtracted from the measurement. Because the blank concentration is closer to the detection limit of the instrument, the imprecision of the blank is large compared with the blank measurement itself. This relationship causes the analytical blank to frequently become the limiting factor in the overall measurement precision.

To compute the overall standard deviation for a final measurement, several sources of error and imprecision must be combined. The standard deviation for each component of the computation of y must be considered when determining the overall measurement uncertainty.

$$y(\pm s_y) = a(\pm s_a) - b(\pm s_b)$$

As shown by the following equation, the standard deviation of the result, s_y is given by combining the standard deviations of the measurements (Reference 6).

$$s_y = \sqrt{s_a^2 + s_b^2 + s_c^2}$$

In this case, "a" represents the standard deviation of the measurement, "b" represents the standard deviation of the blank, that must be subtracted, and "c" represents the uncertainty associated with the sampling error. This example will only consider the uncertainty of the measurement "a" and the blank "b", as the sampling uncertainty "c" is beyond the scope of this discussion (presented previously and may be found in other literature, References 7, 8).

The following example illustrates a common relationship that causes the imprecision of the blank to be the limiting factor in the overall uncertainty of the analysis. Analysis of a set of samples determines the mean value to be 55.5 ± 0.3, with an analytical blank of 11 ± 5 (which is too large to be ignored). The uncertainties of these results are the standard deviations of the replicate measurements. The analytical blank becomes the dominant uncertainty in calculating the uncertainty of the final result. Here the blank subtracted mean y = 55.5 - 11 = 44.5, and the standard deviation is 5.   The net result of the analysis is 44.5 ± 5. Essentially, the entire uncertainty is due to the uncertainty of the analytical blank.

It has been suggested by some environmental laboratories that having a blank concentration below the instrumental detection limit while the measurement is detectable provides a more convenient measurement.   This is, however, not an appropriate approach for minimizing contribution of the blank. A blank value below the limit of detection does not remove its influence. Just because the blank is not detectable does not mean it is not influencing the measurement. An accurate measurement of the blank value with high precision provides the most accurate overall analytical estimate of the concentration.

The four primary areas that effect the analytical blank can be demonstrated using standard reference materials in analysis. Table 3-2 illustrates and isolates the main blank influencing parameters: environment, reagents, materials, and analyst skills. The skill of the analyst was kept constant as the same analyst changed the environment, reagents, and combinations of these

parameters in the analysis (3). Trace elements in glass (TEG) National Institute of Standards and Technology (NIST) standard reference material was used to keep sample homogeneity constant and to permit removal of the sampling error by using sample sizes where appropriate homogeneity had previously been demonstrated.

It is important to note that the relationship of the precision and measurement remained relatively constant. This relationship yields no information about the accuracy of the data. The significance of the first two major sources of contamination, environment and reagents, can be evaluated. In the example above, the contamination in the laboratory air and in the acid used for the reagent blank altered the accuracy of the example above by over two orders of magnitude for both lead and silver. The larger influence of the two sources in this example is the laboratory environment in which the samples were prepared.

The Sample Preparation and Analysis Atmosphere

The laboratory environment in which the sample is prepared is the major source of contamination for most elements. Some rare elements may be an exception, but for the majority of elements of interest, contamination from airborne sources is the most significant of the four main sources. Table 3-3 illustrates concentrations of lead in the air.

This contamination can also be seen in the comparison of 58,000 particles per liter of air measured in a normal laboratory in Pittsburgh, Pennsylvania, and inside a clean chamber in an adjacent laboratory five meters away. Figure 1 demonstrates the dramatic difference between the two environments. Cost effective methods of creating clean chambers for sample preparation are documented along with this data in the references (1).

Any laboratory air that comes in contact with the sample may deposit some portion of its elemental content into the sample. The sample is especially vulnerable to this transfer when it is being decomposed in acid. The acid will leach particles from the air resulting in unwanted ions in solution, mixing with those of the sample.

To prevent air from contaminating the sample, the sample must be processed in a clean environment. This is much easier to accomplish than it may appear at first. These precautions are becoming state-of-the-art in many analytical and environmental laboratories. The prevention of airborne contamination is most frequently dealt with by employing a laminar flow clean bench or a clean laboratory facility. Instructions are referenced for the construction of both from component parts; both are relatively inexpensive and uncomplicated, once the concepts are understood (Ref. 1).

There are many sources of airborne contamination. Several of the sources have been described and their particle size ranges are provided in Figure 2. These diverse sources primarily provide particulates in discrete size ranges. Depending on whether the laboratory is located in an industrial, urban, or rural area, or near the sea, the distribution of these source particles will be different, as will their composition. The vertical dashed line in Figure 2 indicates the particle size cutoff, usually 0.5 µm, for the high efficiency particulate air (HEPA) filter used to prevent particulate contamination. Particles above this size cannot pass through a HEPA filter that is in good working order. These filters were developed jointly by the Massachusetts Institute of Technology and Arthur D. Little & Company, Inc., for the Manhattan Project during World War II and are in common use today (Refs.1, 11).

The definition of clean air is derived from Federal Standard 209a, which defines cleanliness levels. Table 3-4 lists these conditions. "Laminar flow" is directed coherent air movement that does not contain any turbulence.

A dramatic reduction in airborne contaminants can be expected by using HEPA filtered air in laminar flow clean hoods or entire clean laboratories. Table 3-5 demonstrates the dramatic differences in airborne contaminant concentrations in an ordinary laboratory, a clean laboratory, and a clean hood inside a clean laboratory.

Reagent Purity

For acid decomposition, leaching, and extraction, the purity of the reagents used is extremely important to the overall level of the blank. Reagents have very different purities depending on their processing grade and purpose. Frequently, the analyst must purchase special reagents or purify lesser grade reagents prior to use in order to minimize the analytical blank.

In addition to the purity of the reagents, the quantity that must be added is also significant. When reagents are added, they bring with them elemental and molecular components that exist as contaminants. The more reagent that must be used due to reasons other than the stoichiometric reaction, the higher the blank. Reagents of high purity must either be purchased or produced in the laboratory.

In the preparation of high purity reagents, there is only one significant and practical choice for the method of purification. Sub-boiling distillation (Refs. 13, 14), different from normal distillation, uses an infrared radiation source to heat the reagent to a temperature just below the boiling point. Not allowing the reagents to boil prevents the "Brownian movement" of solution droplets produced when bubbles burst at the surface of the liquid. These aerosolized solution particles are carried everywhere in the apparatus and physically transport metal ions and contaminants that should have been left in solution. Sub-boiling distillation is a slower but very reliable method of purifying all of the common mineral acids and many organic reagents used in analytical methods. It relies exclusively on the vapor pressure of the reagent, and contaminant, and can therefore be specifically optimized for purification of the mineral acids if the object is to remove metal ions. Of all acids, nitric acid, for a variety of reasons, can be purified to excellent quality. Because large quantities of reagents are necessary for many laboratories and a continuous supply of these reagents is desirable, methods for constructing a sub-boiling distillation apparatus are provided in the references; sources of these apparatus are also provided. Purchasing sub-boiling acids from commercial sources is also an option (1). Construction or purchase of sub-boiling reagent purification equipment is cost effective depending on the quantity of reagents required.

Materials for Sample Preparation, Storage, and Analysis

For elemental analysis, specific, preferred materials are used for the construction of sample vessels and instrument components that come in contact with the sample. Over the past two decades, materials identified as being non-contaminating have become the top choices for bottles, beakers, reaction vessels, storage containers, nebulizers, and instrument components for trace and ultra-trace analysis. These materials are the same as those currently being used in many digestion vessels, bomb liners, and microwave vessels. These materials are thermally durable, chemically resistant or inert, non-contaminating, and have appropriate compression and tensile strength. Table 3-6 lists the specific types of materials of non-contaminating nature and chemical inertness

to most acid reactions, in order of preference. These materials have been evaluated and tested extensively for their elemental contamination characteristics (Refs. 1-3, 15, 16).

With the exception of polyethylene, these are the most common materials used for sample preparation vessels, both atmospheric pressure vessels and closed vessel liners that come in contact with the sample. These materials are the most stable to acid reactions (with the exception of quartz and glass if hydrofluoric acid is used). Fluoropolymers are the most common and were adapted from other chemical uses for application in pressure systems. The fluoropolymers, TFM, PFA and TFE or PTFE have the highest range of use temperatures of most plastics, ranging from 270 to 300 $^{\circ}$C. They are also chemically inert to the majority of mineral acids and combinations thereof. Sulfuric acid has a boiling point of approximately 330 $^{\circ}$C and can damage all fluoropolymers by melting them. Quartz and glass can safely contain sulfuric acid at these high temperatures, but borosilicate glass is not appropriate for ultra-trace elemental analysis (Refs. 3, 15). Glass actually forms a gel layer that hydrates and leaches, transferring elemental components from the glass to the sample solution. While these are minute quantities, there are many low level analyses where these contributions would be detected in the blank and the sample.

Polyethylene is suitable for storage of diluted samples after decomposition, but it does not have a thermal use temperature appropriate for decomposition. It is also not sufficiently inert to be useful as a decomposition vessel or vessel liner, similar to polycarbonate and polypropylene. The low cost of polyethylene and its relative inertness to cool, weakly acidic solutions make it an excellent storage container for trace element solutions (Ref. 1).

Analytical Technique and Synergistic Equipment

The fourth significant source of analytical blank contamination is the skill of the analyst and the appropriateness of the technique that is being performed. Analytical blank control has been explained as the combination of atmosphere, reagent, material, and the protocol being used correctly. Here the skill and awareness of the analyst and the way in which combinations of the aforementioned clean chemistry tools are applied is significant to the final result of contamination and analytical blank control. Sample preparation instrumentation may also assist in these protocols. For example, microwave sample preparation assists each of these parameters in synergistic ways, thus lowering the analytical blank, improving blank precision, and enhancing overall quality control and transferability of methods. Some instrumentation and fundamental processes involved in specific sample preparation procedures assists the analyst by incorporating useful clean chemistry concepts into instrumentation and method structure. Such instrumentation is pertinent since microwave methods now exist that provide sample preparation for leaching or total analysis of all elements simultaneously. Analyst skill involving clean chemistry is assisted by the method structure and microwave equipment as indicated below.

- If a closed or controlled atmospheric microwave vessel is prepared in a clean hood and sealed before leaving the clean environment, the sample will not be affected by atmospheric contamination during the reaction, since it has not been removed from a clean environment.

- The vessel materials described would not normally be used by many laboratories that can benefit, so the advantages of the fluoropolymers would not be realized if they were not required in most microwave reaction vessels.

·	The time the sample spends in decomposition, leaching, or extraction is typically reduced from hours to minutes, thus reducing the potential leaching from the container walls

·	Because most microwave systems are sealed systems, evaporation of the reagent before it reacts productively is prevented and smaller quantities of reagents are used thus preventing excess blank accumulation.

The blank is reduced in size and is more consistent due to limiting the exposure variables. An example of the these components working together has been provided in the literature where analysis under different conditions has verified these conclusions (Refs. 1, 18, 19). The example illustrates the isolation of the blank optimization areas: environment, reagents, materials, and analysis skills. The skill of the analyst is kept more constant as the instrument dictates more clean, chemically appropriate procedures.

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TABLE 3-1.

SAMPLE HOLDING TIMES, RECOMMENDED DIGESTION VOLUMES AND
RECOMMENDED COLLECTION VOLUMES FOR INORGANIC
DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES

Measurement	Digestion Volume. (mL)[a, c]	Collection Volume (mL)[a,c]	Treatment/ Preservative Holding Time[b]
Inorganic Analytes (except hexavalent chromium and mercury):			
Aqueous			
Total	100	600	HNO_3 to pH <2 6 months
Dissolved	100	600	Filter on site; HNO_3 to pH <2 6 months
Suspended	100	600	Filter on site 6 months
Solid			
Total	2 g	200 g	6 months
Hexavalent Chromium:			
Aqueous	100	400	24 hours Store at 4°± 2°C until analyzed
Solid	2.5 g	100 g	One month to extraction, 4 days after extraction Store at 4°± 2°C until analyzed
Mercury:			
Aqueous			
Total	100	400	HNO_3 to pH <2 28 days
Dissolved	100	400	Filter; HNO_3 to pH <2 28 days
Solid			
Total	0.2 g	200 g	28 days Store at 4°± 2°C until analyzed

[a]   Unless stated otherwise.
[b]   Either glass or plastic containers may be used.
[c]   Any sample volume reduction from the reference method's instructions must be made in the exact proportion as described in the method and representative sampling must be maintained.

TABLE 3-2

EXAMPLES OF THE ANALYTICAL BLANK INFLUENCE
ON TRACE ANALYSIS OF ELEMENTS IN GLASS (Ref. 3)

CONDITIONS	Pb (ng)	Ag (ng)
Initial analysis of TEG* standard	330±250	970±500
Analysis using sub-boiled distilled acids	260±200	------------
Analysis in class 100 hood	20±8	207±200
Analysis using sub-boiled acids in class 100 hood	2±1	3±2

* TEG - Trace Element in glass, SUMS 610 - 619, ± s.

TABLE 3-3

EXAMPLES OF LEAD CONCENTRATIONS IN AIR

SITE	LEAD CONCENTRATION ($\mu g\ m^{-3}$)
Downtown Air, St. Louis, MO	18.84 (Ref. 9)
Rural Park Air, Southeastern MO	0.77 (Ref. 10)
Laboratory Air, NIST, MD	0.4 (Ref.3)

TABLE 3-4

CLEANLINESS LEVELS IN FEDERAL STANDARD 209a (Ref. 11)

CLASS[A]	MAXIMUM CONTAMINATION IN WORK AREA (particles ft^{-3})
100	100 particles > 0.5 µm 0 particles > 5.0 µm
10,000	10,000 particles > 0.5 µm 65 particles > 5.0 µm
100,000	100,000 particles > 0.5 µm 700 particles > 5.0 µm

[A]The standard required laminar-flow equipment to attain this level of cleanliness.
Since measurement of dust particles smaller than 0.5 µm introduces substantial errors, 0.5 µm has been adopted as the criterion of measurement.

TABLE 3-5

PARTICULATE CONCENTRATIONS IN LABORATORY AIR (Ref. 10)

SITE	CONCENTRATION (µg m^{-3})			
	Iron	Copper	Lead	Cadmium
Ordinary Laboratory	0.2	0.02	0.4	0.002
Clean Room	0.001	0.002	0.0002	ND
Clean Hood	0.0009	0.007	0.0003	0.0002

ND - Not Detected

TABLE 3-6

NON-CONTAMINATING MATERIALS AND SPECIFICATION FOR USE
IN ULTRA-TRACE ANALYSIS AND AS DECOMPOSITION
VESSELS AND SAMPLE CONTAINERS (Ref. 11)

Listed from highest to lowest preference for use in sample containment

Fluoropolymers: PFA*, TFM, TFE*, FEP*, Tefzel*

Quartz - Synthetic

Polyethylene (suitable for storgage only, not for acid digestion)

Quartz - Natural

Borosilicate Glass

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* Various forms of Teflon®

FIGURE 1

COMPARISON OF PARTICLE COUNT ANALYSIS, COUNTS VS. PARTICLE SIZE, OF A
CLEAN ROOM AND A STANDARD LABORATORY AT DUQUESNE UNIVERSITY
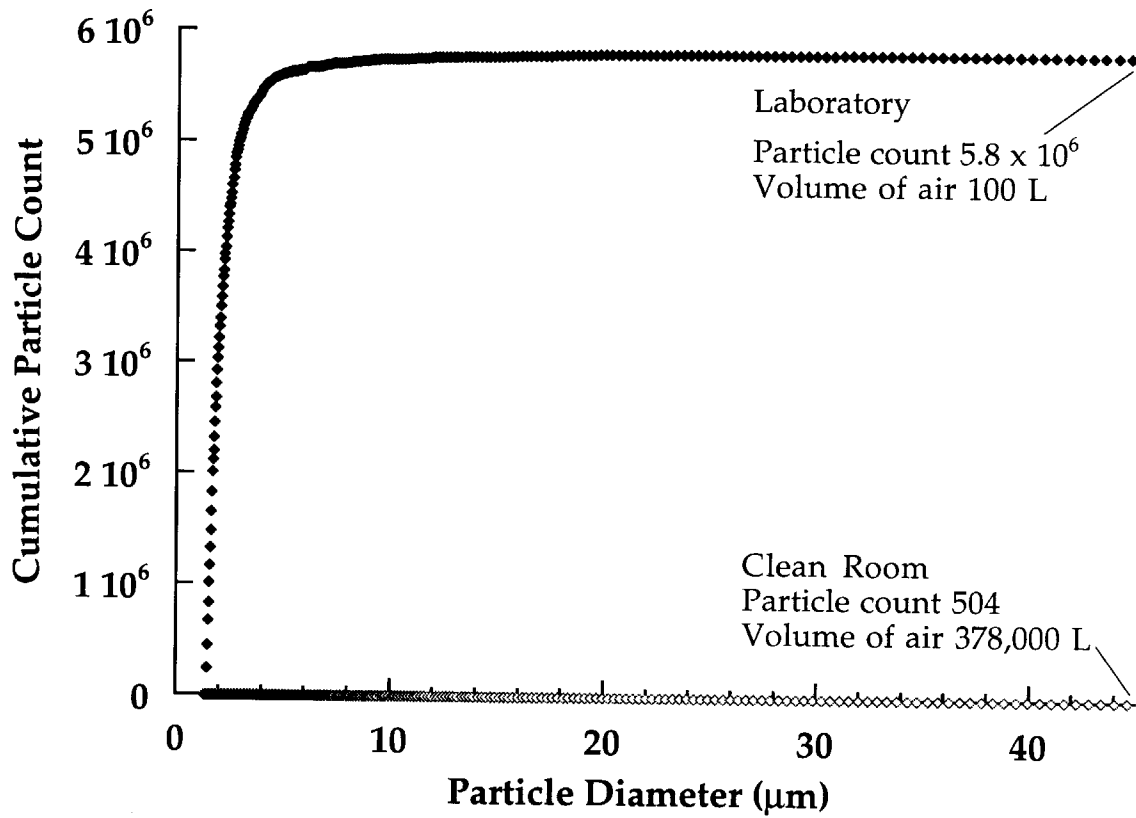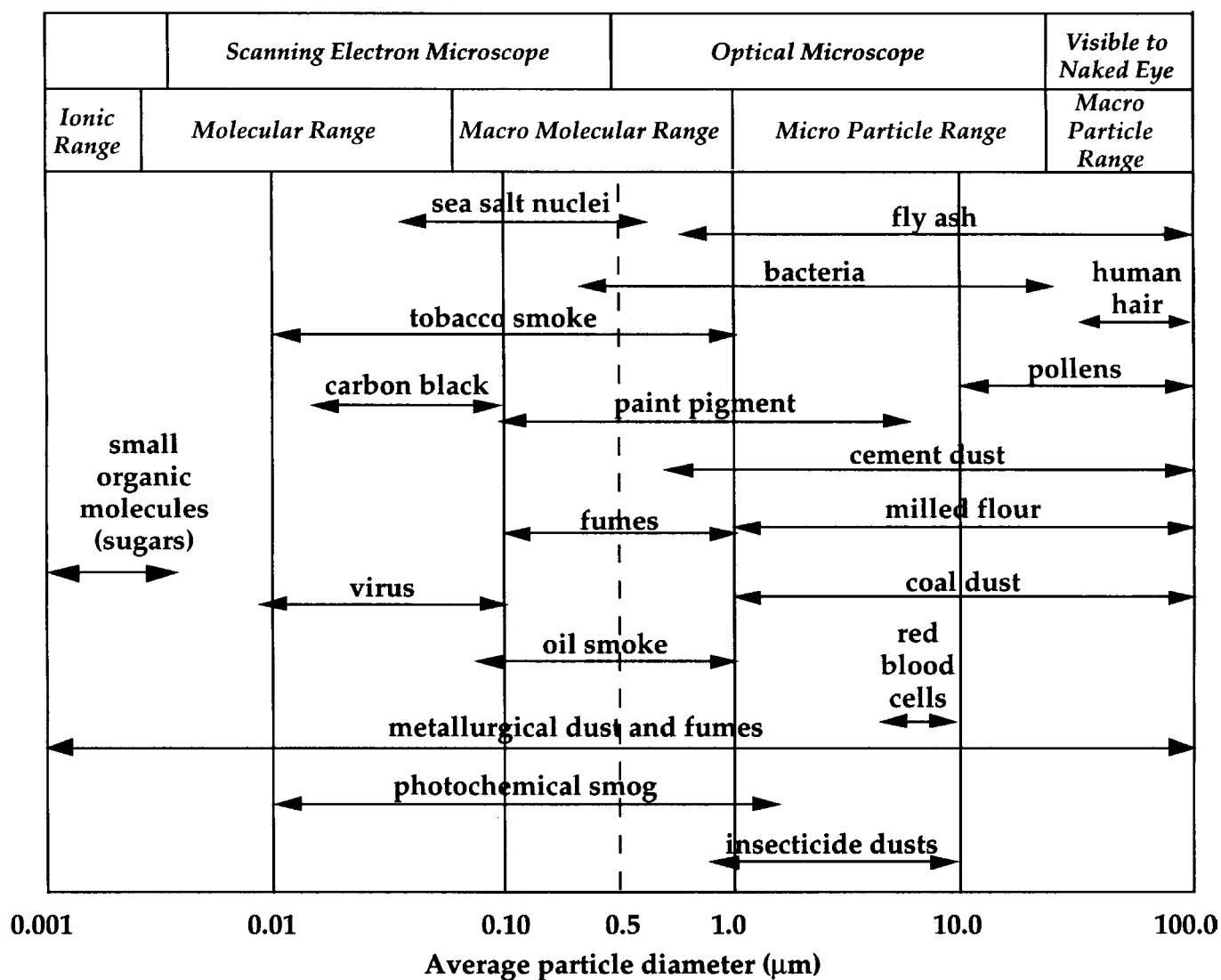IN PITTSBURGH, PA (Ref. 1)

FIGURE 2

PARTICLE SIZE COMPARISON CHART FOR COMMON PARTICULATES (Refs. 1, 12)

	Scanning Electron Microscope		Optical Microscope	Visible to Naked Eye
Ionic Range	Molecular Range	Macro Molecular Range	Micro Particle Range	Macro Particle Range

sea salt nuclei

fly ash

bacteria

human hair

tobacco smoke

carbon black

pollens

paint pigment

small organic molecules (sugars)

cement dust

fumes

milled flour

virus

coal dust

oil smoke

red blood cells

metallurgical dust and fumes

photochemical smog

insecticide dusts

0.001   0.01   0.10   0.5   1.0   10.0   100.0

Average particle diameter (μm)

3.2 SAMPLE DIGESTION METHODS

The methods in SW-846 for sample digestion or dissolution are as follows[1]:

Method 3005 prepares ground water and surface water samples for total recoverable and dissolved metal determinations by FLAA, ICP-AES, or ICP-MS. The unfiltered or filtered sample is heated with dilute HCl and HNO_3 prior to metal determination.

Method 3010 prepares waste samples for total recoverable metal determinations by FLAA, ICP-AES, or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with hydrochloric acid. The method is applicable to aqueous samples, leachates, and mobility-procedure extracts.

Method 3015 prepares aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total recoverable metal determinations by FLAA, GFAA, ICP-AES, or ICP-MS. Nitric acid and hydrochloric acid are added to the sample in a Teflon digestion vessel and heated in a microwave unit prior to metals determination.

Method 3020 prepares waste samples for total recoverable metals determinations by furnace GFAA or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with nitric acid. The method is applicable to aqueous samples, leachates, and mobility-procedure extracts.

Method 3031 prepares waste oils, oil sludges, tars, waxes, paints, paint sludges and other viscous petroleum products for analysis by FLAA, GFAA, and ICP-AES. The samples are vigorously digested with nitric acid, sulfuric acid, hydrochloric acid, and potassium permanganate prior to analysis.

Method 3040 prepares oily waste samples for determination of soluble metals by FLAA, and ICP-AES methods. The samples are dissolved and diluted in organic solvent prior to analysis. The method is applicable to the organic extract in the oily waste EP procedure and other samples high in oil, grease, or wax content.

Method 3050 prepares waste samples for total recoverable metals determinations by FLAA and ICP-AES, or GFAA and ICP-MS depending on the options chosen. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. The method is applicable to soils, sludges, and solid waste samples.

Method 3051 prepares sludges, sediments, soils and oils for total recoverable metal determinations by FLAA, GFAA, ICP-AES or ICP-MS. Nitric acid and hydrochloric acid are added to the representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to metals determination.

Method 3052 prepares siliceous and organically based matrices including ash, biological tissue, oil, oil contaminated soil, sediment, sludge, and soil for total analysis by FLAA, CVAA, GFAA, ICP-

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[1] Please note that chlorine is an interferant in ICP-MS analyses and its use should be discouraged except when absolutely necessary.

AES, and ICP-MS. Nitric acid and hydrofluoric acid are added to a representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to analysis.

Method 3060 prepares soils, sludges, sediments and similar waste materials for hexavalent chromium determination. The samples are digested and heated to dissolve the Cr(VI) and stabilize it against reduction to Cr(III).

Prior to employing the above methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

3.3 METHODS FOR DETERMINATION OF INORGANIC ANALYTES

     This section of the manual contains analytical techniques for trace inorganic analyte determinations. Examples of the techniques included in this section are: inductively coupled argon plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), direct-aspiration or flame atomic absorption spectrophotometry (FLAA), graphite-furnace atomic absorption spectrophotometry (GFAA), hydride-generation atomic absorption spectrometry (HGAA), cold-vapor atomic absorption spectrometry (CVAA), and several procedures for hexavalent chromium analysis. Each of these is briefly discussed below in terms of advantages, disadvantages, and cautions for analysis of wastes.

     ICP allows simultaneous or rapid sequential determination of many elements in a short time. A primary disadvantage of ICP is the occurrance of background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and back-ground correction to minimize these interferences, analysis for traces of inorganic analytes in the presence of a large excess of a single analyte is difficult. Examples would be traces of inorganic analytes in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FLAA. Detection limits are drastically improved when ICP-MS is used. In general ICP-MS exhibits greater sensitivity than either GFAA or FLAA for most elements. The greatest disadvantage of ICP-MS is isobaric elemental interferences. These are caused by different elements forming atomic ions with the same nominal mass-to-charge ratio. Mathematical correction for interfering ions can minimize these interferences.

     Flame AAS (FLAA) direct aspiration determinations, as opposed to ICP, are normally completed as single element analyses and are relatively free of interelement spectral interferences. Either a nitrous-oxide/acetylene or air/acetylene flame is used as an energy source for dissociating the aspirated sample into the free atomic state, making analyte atoms available for absorption of light. In the analysis of some elements, the temperature or type of flame used is critical. If the proper flame and analytical conditions are not used, chemical and ionization interferences can occur.

     Graphite furnace AAS (GFAA) replaces the flame with an electrically heated graphite furnace. The furnace allows for gradual heating of the sample aliquot in several stages. Thus, the processes of dissolution, drying, decomposition of organic and inorganic molecules and salts, and formation of atoms which must occur in a flame or ICP in a few milliseconds may be allowed to occur over a much longer time period and at controlled temperatures in the furnace. This allows an experienced analyst to remove unwanted matrix components by using temperature programming and/or matrix modifiers. The major advantage of this technique is that it affords extremely low detection limits. It is the easiest to perform on relatively clean samples. Because this technique is so sensitive, interferences can be a real problem; finding the optimum combination of digestion, heating times and temperatures, and matrix modifiers can be a challenge for complex matrices.

     Hydride AA utilizes a chemical reduction to reduce and separate arsenic or selenium selectively from a sample digestate. The technique therefore has the advantage of being able to isolate these two elements from complex samples which may cause interferences for other analytical procedures. Significant interferences have been reported when any of the following is present: (1)

easily reduced metals (Cu, Ag, Hg); (2) high concentrations of transition metals (>200 mg/L); (3) oxidizing agents (oxides of nitrogen) remaining following sample digestion.

Cold-Vapor AA uses a chemical reduction to reduce mercury selectively. The procedure is extremely sensitive but is subject to interferences from some volatile organics, chlorine, and sulfur compounds.

Prior to employing the above methods in this chapter, analysts are advised to consult the disclaimer statement at the front of this manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in each procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgements necessary to meet the data quality objectives or needs for the intended use of the data.

The following methods are included in this section:

Method 4500:	Mercury in Soil by Immunoassay
Method 6010B:	Inductively Coupled Plasma-Atomic Emission Spectrometry
Method 6020A:	Inductively Coupled Plasma - Mass Spectrometry
Method 6200:	Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment
Method 6500:	Dissolved Inorganic Anions in Aqueous Matrices by Capillary Ion Electrophoresis
Method 6800:	Elemental and Speciated Isotope Dilution Mass Spectrometry
Method 7000B:	Flame Atomic Absorption Spectrophotometry
Method 7010:	Graphite Furnace Atomic Absorption Spectrophotometry
Method 7061A:	Arsenic (Atomic Absorption, Gaseous Hydride)
Method 7062:	Antimony and Arsenic (Atomic Absorption, Borohydride Reduction)
Method 7063:	Arsenic in Aqueous Samples and Extracts by Anodic Stripping Voltammetry (ASV)
Method 7195:	Chromium, Hexavalent (Coprecipitation)
Method 7196A:	Chromium, Hexavalent (Colorimetric)
Method 7197:	Chromium, Hexavalent (Chelation/Extraction)
Method 7198:	Chromium, Hexavalent (Differential Pulse Polarography)
Method 7199:	Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography
Method 7470A:	Mercury in Liquid Waste (Manual Cold-Vapor Technique)
Method 7471B:	Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)
Method 7472:	Mercury in Aqueous Samples and Extracts by Anodic Stripping Voltammetry (ASV)
Method 7473:	Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry
Method 7474:	Mercury in Sediment and Tissue Samples by Atomic Fluorescence Spectrometry
Method 7580:	White Phosphorus (P_4) by Solvent Extraction and Gas Chromatography
Method 7741A:	Selenium (Atomic Absorption, Gaseous Hydride)
Method 7742:	Selenium (Atomic Absorption, Borohydride Reduction)

Method 9000: Determination of Water in Waste Materials by Karl Fischer Titration

Method 9001: Determination of Water in Waste Materials by Quantitative Calcium Hydride Reaction